

μ -Oxo Bridged Heterometal Phthalocyanine Compound and
Selective Production Method Thereof

Field of the Invention

5 The present invention relates to a novel μ -oxo bridged
heterometal phthalocyanine compound which is useful for
electric charge generating materials such as organic
photoreceptors, photoconductive materials, optical
recording materials, organic solar cell materials,
10 nonlinear optical materials and the like, and to a
production method thereof.

Description of the related Art

15 Metal phthalocyanine-based compounds have been noted
as organic photoconductive substances having sensitivity
around a wavelength of 800 nm which is an oscillation
wavelength range of a semiconductor laser. A number of
organic photoreceptors (OPC) including such organic
photoconductive substances as effective components have
20 been proposed. For example, organic photoreceptors
employing titanylphthalocyanine-based compounds as electric
charge generating materials have been made to practical use.

25 Recently, medium-to-high sensitive electric charge
generating materials provided with a new performance, that
are suitable for the shortwaving of a light source by the

prevalence of light-emitting diodes (LED) and OPC for color laser-beam printers (LBP), have been vigorously searched.

It has been known that phthalocyanine (Pc) compounds generate electric charge by exposing to light and show
5 various electrical properties depending upon polymorphs thereof, presence or absence of central metal, kind of central metal thereof, and the like.

For example, with regard to a mixed crystal of two or more kinds of phthalocyanine compounds, Japanese Patent
10 Kokai Publication No. H2(1990) 272067 discloses a method for preparing an X-type metal-free phthalocyanine composition, wherein titanylphthalocyanine is added to a metal-free phthalocyanine in an amount equal or less than that of the metal-free phthalocyanine and mixed to conduct
15 crystal transformation. Japanese Patent Kokai Publication No. H4(1992) 351673 also discloses a mixed crystal of oxytitanium phthalocyanine and at least one kind of hydroxymetal phthalocyanine. Japanese Patent Kokai Publication No. H4(1992) 184452 discloses a coating
20 solution for photoreceptors, which contains titanylphthalocyanine and a multilayer-type phthalocyanine derivative. Japanese Patent Kokai Publication No. H8(1996) 67829 discloses a method for preparing a phthalocyanine mixed crystal, which comprises: dissolving at least two
25 kinds of phthalocyanine-based compounds in acid; and adding

this solution to a mixture solution of water and an organic solvent having a dielectric constant of 20 or less so as to precipitate as the phthalocyanine mixed crystal. Japanese Patent Kokai Publication No. 2002-12790 discloses a mixed
5 crystal of at least three kinds of phthalocyanine each having different central substance.

Further, Japanese Patent Kokai Publication No. H9(1997) 217020 discloses a μ -oxo aluminum phthalocyanine dimer having a new polymorph, and Japanese Patent Kokai
10 Publication No. H10(1998) 88023 discloses a μ -oxo gallium phthalocyanine dimer. In addition, Japanese Patent Kokai Publication No. H7(1995) 295259 discloses an alkoxy bridged metal phthalocyanine dimer.

Japanese Patent Kokai Publication No. H6(1994) 145550
15 discloses a process, which includes the step of mixing a titanylphthalocyanine with a halogenated metal phthalocyanine having metal (III) as central metal thereof, and reprecipitating the mixture by acid pasting treatment in water. However, the reference does not describe μ -oxo
20 bridged compounds, or selective production method thereof.

With regard to a μ -oxo heterometal phthalocyanine dimer, Japanese Patent Kokai Publication No. 2000-219817 discloses a μ -oxo aluminum/gallium phthalocyanine dimer. The phthalocyanine dimer described therein, however, is
25 inevitably obtained in the form of a mixture of three kinds

which contains a μ -oxo aluminum phthalocyanine dimer, and a μ -oxo gallium phthalocyanine dimer in addition to μ -oxo aluminum/gallium phthalocyanine dimer.

Further, United States Patent No. 4900817 discloses a
5 polycyclic phthalocyanine compound such as $(\text{HO})\text{GePc-O-SiPcOSi}(\text{C}_6\text{H}_{13})_3$. The polycyclic phthalocyanine compound, however, has tetravalent Si and Ge as central metal thereof. In addition, a production method thereof is based on
dehydration of hydroxy-substituted metal(IV) phthalocyanine
10 in an organic solvent.

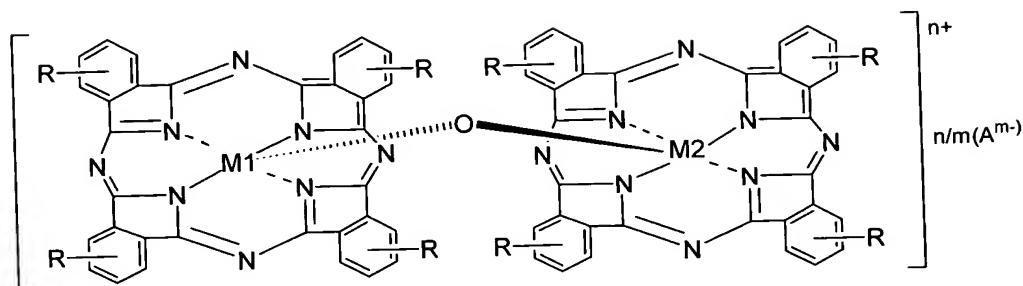
Summary of the Invention

It is an object of the present invention to provide a novel μ -oxo bridged heterometal phthalocyanine compound,
15 which can provide an organic photoreceptor having diversified properties, e. g. optical sensitivity or electric property to use the materials as charge generating materials.

It is another object of the present invention to
20 provide a method for preparing the μ -oxo bridged heterometal phthalocyanine compound, which allows a simple production of the compound with excellent selectivity and high yield.

More specifically, the present invention provides a μ -
25 oxo bridged heterometal phthalocyanine compound represented

by the following formula I:



I

wherein M1 represents a metal atom which is able to have a
 5 valence of up to three, excepting indium (In), M2
 represents a metal atom which is able to have a valence of
 four, R represents each independently one or more
 substituent groups and/or substituent atoms, (A^{m-})
 represents a counteranion A having a valence of m, n/m
 10 represents the number of the counteranion, n represents an
 integer selected from 0 or 1 to 3 corresponding to a
 valence of M2, and m represents 1 or 2.

The present invention also provides a method for
 preparing a μ -oxo bridged heterometal phthalocyanine
 15 compound, which comprises the step of reacting
 phthalocyanine having halometal (III) as central metal
 thereof with phthalocyanine having oxymetal(IV) as central
 metal thereof, respectively, in equimolar amount, and
 washing the resultant compound with aqueous ammonia.

20

Brief Description of Drawings

Fig. 1 is a XRD spectrum of Example 1;
Fig. 2 is a TOF-MS spectrum of Example 1;
Fig. 3 is a XRD spectrum of Example 2;
Fig. 4 is a TOF-MS spectrum of Example 2;
5 Fig. 5 is a XRD spectrum of Example 4;
Fig. 6 is a TOF-MS spectrum of Example 4;
Fig. 7 is a TOF-MS spectrum of Example 6;
Fig. 8 is a TOF-MS spectrum of Example 7;
Fig. 9 is a ^1H -HNR spectrum of Example 7;
10 Fig. 10 is a ^{13}C -NMR spectrum of Example 7;
Fig. 11 is an IR spectrum of Comparative Example 7;
Fig. 12 is a near-ultraviolet visible near-infrared
absorption of Example 7; and
Fig. 13 is a TOF-MS spectrum of Comparative Example 2.

15

Detailed Description of the Invention

A μ -oxo bridged heterometal phthalocyanine compounds
of the present invention has a structure in which the
central metal atom (M1) in a metal phthalocyanine including
20 M1 as central metal thereof is oxo-bridged with the central
metal M2 in a metal phthalocyanine including M2 as central
metal thereof. M1 means a metal atom which is able to have
a valence of up to three and, for example, involves a metal
atom of the 3A group (such as Sc and Y) or the 3B group
25 (such as Al, Ga, In and Tl) on the periodic table. M2

means a metal atom which is able to have a valence of four and, for example, involves a metal atom of the 4A to 7A groups, the 8 group and the 4B to 6B groups on the periodic table. A metal atom of the 3A group or the 3B group on the periodic table (such as Al and Ga) is not included in M2. Meanwhile, M2 may exist as a trivalent form when it is included in the structure of the μ -oxo bridged heterometal phthalocyanine compound.

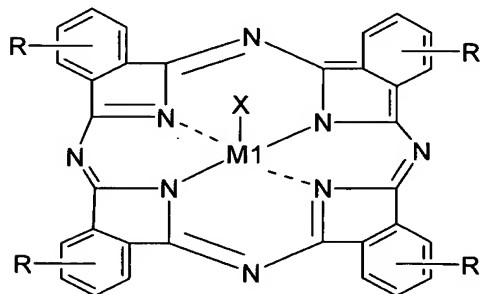
The μ -oxo bridged heterometal phthalocyanine compound of the present invention may have one or more substituent groups and/or substituent atoms (R) on the aromatic rings thereof. The kind of the substituent groups and the substituent atoms is not particularly limited as long as it exists with stability in the compounds, and specific examples thereof include an alkyl group (such as a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, a tert-butyl group and an isoamyl group), an alkoxy group (such as a methoxy group, an ethoxy group, an isopropoxy group and a butoxy group), a phenoxy group, an aryl group (such as a phenyl group and a tolyl group), an aralkyl group (such as a benzyl group), an allyl group, an alkenyl group, a cyano group, a halogen atom (such as Cl, Br, I and F), a carboxylate group, a sulfonate group, a nitro group, an amino group, and the like.

In addition, the μ -oxo bridged heterometal

phthalocyanine compound of the present invention may carry positive charge ($n+$) corresponding to a valence of central metal atom ($M2$) and, therefore, typically exists in a form of being accompanied by a suitable counteranion (A) in a solution. Examples of the counteranion (A) include a monovalent inorganic anion such as hydroxy ion (OH^-), halogen ion (for example, Cl^-) and hydrogen sulfate ion (HSO_3^-), or a divalent inorganic anion such as sulfate ion. A preferable counteranion (A) is a hydroxy ion (OH^-) as in the case of washing with aqueous ammonia after reacting.

The μ -oxo bridged heterometal phthalocyanine compound is produced by reacting phthalocyanine having halometal (III) as central metal thereof (hereinafter, referred to as halometal(III) phthalocyanine) with phthalocyanine having oxymetal(IV) as central metal thereof (hereinafter, referred to as oxymetal(IV) phthalocyanine).

Halometal(III) phthalocyanine is represented, for example, by the following formula A:



A

wherein R and M1 have the same meanings as defined above,

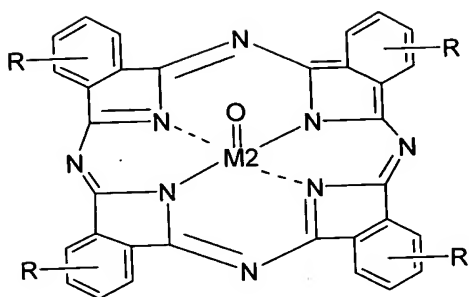
and X represents a halogen atom.

Halometal(III) phthalocyanine can be obtained by using a well-known method. The method includes, for example, reacting phthalonitrile, 1,3-diimino isoindoline or derivatives thereof with a halide of trivalent metal atom in an organic solvent with high-boiling point such as 1-chloronaphthalene or quinoline. In addition, the product may optionally be filtered under heating and washed with hot DMF, DMF and the like. A halogen atom of the halide includes fluorine, chlorine, bromine or iodine, chlorine being preferred.

Preferable examples of central metal atom M1 of the halometal(III) phthalocyanine include aluminum Al(III) and gallium Ga(III). Indium In(III), however, is not preferred as M1. In case of a halometal(III) phthalocyanine having a central metal of Indium, Indium is easily eliminated from a phthalocyanine ring to produce a metal-free phthalocyanine as a side reaction. This side reaction would make the occurrence of the reaction of the present invention difficult.

Examples of halometal(III) phthalocyanine preferably include chlorogallium phthalocyanine and chloroaluminum phthalocyanine.

Oxymetal(IV) phthalocyanine is represented, for example, by the following formula B:



B

wherein R and M2 have the same meanings as defined above.

Oxymetal(IV) phthalocyanine can be obtained by using a well-known method. The method includes, for example, reacting phthalonitrile, 1,3-diimino isoindoline or a derivative thereof together with a halide of metal atom having a valence of three to six (such as titanium chloride, vanadyl chloride and molybdenum chloride) in an organic solvent with high-boiling point such as 1-chloronaphthalene or quinoline and, to hydrolyze the obtained metal (di)halide phthalocyanine. The hydrolysis may start by washing with DMF and the like, but the reaction is preferably conducted in dilute hydrochloric acid as required.

Examples of central metal atom M2 of the oxymetal(IV) phthalocyanine include titanium Ti, vanadium V, molybdenum Mo, palladium Pd and the like. Preferable oxymetal(IV) phthalocyanine is titanyl phthalocyanine $O=TiPc$, vanadyl phthalocyanine $O=VPc$, oxymolybdenum phthalocyanine $O=MoPc$. Preferable oxymetal(IV) phthalocyanine includes titanyl

phthalocyanine $O=TiPc$, vanadyl phthalocyanine $O=VPc$, and oxymolybdenum phthalocyanine $O=MoPc$. In particular, titanyl phthalocyanine is preferable.

For example, titanyl phthalocyanine can be generally obtained by reacting phthalonitrile or 1,3-diiminoisoindoline with titanium chloride (such as titanium tetrachloride) in an organic solvent with high-boiling point such as 1-chloronaphthalene or quinoline and, then, hydrolyzing the obtained chlorotitanium phthalocyanine. Alternatively, the titanyl phthalocyanine can be generally obtained by heat-refluxing phthalonitrile and titanium tetrachloride in an alcohol solvent in the presence of a proton-accepting reaction accelerator (such as 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) or 1,5-diazabicyclo[4,3,0]-5-nonene (DBN)), and hydrolyzing the obtained dichlorotitanium phthalocyanine in dilute hydrochloric acid. (Japanese Patent Kokai Publication No. H3(1991) 21669).

The μ -oxo bridged heterometal phthalocyanine compound of the present invention can be produced by reacting the halometal(III) phthalocyanine with oxymetal(IV) phthalocyanine. Halometal(III) phthalocyanine and oxymetal(IV) phthalocyanine are preferably reacted in a molar ratio of 1 to 1, namely, equimolar ratio, which produces the objective μ -oxo bridged heterometal

phthalocyanine compound in high yield.

The reaction includes, for example, a method in which
halometal(III) phthalocyanine is reacted with oxymetal(IV)
phthalocyanine by mixing in an equimolar ratio in the
5 presence of concentrated sulfuric acid. As the
concentrated sulfuric acid, a concentration of 95% or more
is preferred.

Specifically, halometal(III) phthalocyanine can be
reacted with oxymetal(IV) phthalocyanine for 2 to 3 hours
10 by dissolving in concentrated sulfuric acid under the
conditions of cooling (such as a temperature of 5°C or
less). After completion of the reaction, the reacted
compound can be poured onto a large quantity of water/ice
to precipitate. The above operation can finely disperse
15 and purify the resulting compound.

The treatment wherein reaction products and the like
are dissolved in concentrated sulfuric acid, and then
poured onto water/ice to precipitate solid material so as
to be finely divided and refined, is referred to as "acid
20 pasting treatment". In the present invention, according to
the so-called acid pasting treatment, halometal(III)
phthalocyanine is reacted with oxymetal(IV) phthalocyanine
to obtain the μ -oxo bridged heterometal phthalocyanine
compound.

25 After the reaction, the obtained compound is treated

with aqueous ammonia to remove an acid root from the reacted compound easily. Specifically, the reacted compound is added to a mixture of water and ammonia solution and filtered, and the filtered-out compound is sufficiently washed with water and ion exchange water, followed by drying to refine the compound easily. The aqueous ammonia to be suitably used may have a concentration of 1% or more, preferably 5 to 50%, and the aqueous ammonia having a concentration of 25% is more preferably used.

This method enables the μ -oxo bridged heterometal phthalocyanine compound of the present invention to be produced simply, selectively and with high yield.

Examples of the preferable combination of halometal(III) phthalocyanine/oxymetal(IV) phthalocyanine for producing a μ -oxo bridged heterometal phthalocyanine compound of the present invention include chlorogallium phthalocyanine/titanyl phthalocyanine, chlorogallium phthalocyanine/vanadyl phthalocyanine, chloroaluminum phthalocyanine/oxymolybdenum phthalocyanine, chloroaluminum phthalocyanine/titanyl phthalocyanine, chloroaluminum phthalocyanine/oxymolybdenum phthalocyanine, chlorogallium phthalocyanine/oxypalladium phthalocyanine, and the like. Further, the halometal(III) phthalocyanine/oxymetal(IV) phthalocyanine may have one or more substituent groups

and/or substituent atoms on the aromatic rings thereof.

The μ -oxo bridged heterometal phthalocyanine compound thus obtained of the present invention is useful for electric charge generating materials such as organic photoreceptors, photoconductive materials, optical recording materials, organic solar cell materials, nonlinear optical materials and the like.

Advantageous Effect of the Invention

The present invention can provide a μ -oxo bridged heterometal phthalocyanine compound without difficulty, which is a "D- σ -A type dyestuff" in which a donor dyestuff (D) is connected with an acceptor dyestuff (A) through σ -bond. In conventional method, the D- σ -A type dyestuff is obtained by separating and refining from a mixture, because of difficulty of selective production. The μ -oxo bridged heterometal phthalocyanine compound is useful for electric charge generating materials such as organic photoreceptors, photoconductive materials, optical recording materials, organic solar cell materials, nonlinear optical materials and the like. In addition, the present invention can provide a method for preparing a μ -oxo bridged heterometal phthalocyanine compound, which comprises reacting halometal(III) phthalocyanine with oxymetal(IV) phthalocyanine and allows a preparation of the compound

with simple, selective and high yield. The μ -oxo bridged heterometal phthalocyanine compound is able to univocally induce the polarization of intramolecular electronic state.

5 Examples

The following Examples further illustrate the present invention in detail but are not to be construed to limit the scope thereof.

10 Synthesis Example 1

Synthesis of titanyl phthalocyanine

(A method described in Example 1 of Japanese Patent Kokai Publication No. H3(1991) 21669)

1,8-Diazabicyclo[5,4,0]unde-7-cene (DBU) (91.8 g, approximately 0.6 mol) was dropped into a mixture of 76.2 g (approximately 0.6 mol) of phthalonitrile, 56.4 g (approximately 0.3 mol) of titanium tetrachloride and 200 ml of n-amyl alcohol under heat-reflux for approximately 1 hour, and then stirred under heat-reflux for 6 hours.

20 After the reaction was completed, the mixture was allowed to cool to a temperature of 100°C, and approximately 30 ml of water was added thereto, stirred for a while.

Thereafter the product was filtered, sprinkled and washed with 100 ml of dimethylformamide (DMF) and subsequently 100

25 ml of methanol. The obtained dichlorotitanium

phthalocyanine was dispersed into 1000 ml of 3%-
hydrochloric acid and washed with water until pH reached to
6 or more. The resultant water-wet cake was then put into
approximately 500 ml of DMF which had been heated to a
5 temperature of 100 to 120°C, stirred at the temperature for
approximately 1 hour, and thereafter filtered under heating.
The obtained DMF-wet cake was washed with 100 ml of
methanol, and dried to obtain 29.1 g of titanyl
phthalocyanine O=TiPc.

10

Synthesis Example 2

Synthesis of vanadyl phthalocyanine

(A method described in Synthesis Example 1 of Japanese
Patent Kokai Publication No. H7(1995) 247442)

15 Phthalonitrile (32.5 g) and 10.0 g of vanadium
trichloride were reacted in 125 g of quinoline for 5 or 6
hours at 235°C. The obtained product was filtered out and
washed with 200 ml of dimethylformamide (DMF), and
optionally hydrolyzed with dilute hydrochloric acid, to
20 obtain 19.0 g of vanadyl phthalocyanine O=VPc.

Synthesis Example 3

Synthesis of oxymolybdenum phthalocyanine

(A method described in Example 2 of Japanese Patent Kokai
25 Publication No. H8(1996) 60021)

Phthalonitrile (25.6 g) and 10.0 g of molybdenum trichloride were reacted in 150 ml of 1-chloronaphthalene for 5 hours. After the completion of the reaction, the obtained product was filtered under heating, and the
5 obtained cake was sprinkled and washed with dimethylformamide. Then, the obtained product was dispersed again into 120 ml of DMF, stirred and refluxed for 5 hours, and thereafter was filtered under heating. The obtained product was washed with methanol and
10 optionally hydrolyzed with dilute hydrochloric acid to obtain 15.5 g of oxymolybdenum phthalocyanine $O=MoPc$.

Synthesis Example 4

Synthesis of chlorogallium phthalocyanine

15 (A method described in Synthesis Example 1 of Japanese Patent Kokai Publication No. H10(1998) 88023)

Phthalonitrile (145.5 g, (1.13 mol)), 680 ml of 1-chloronaphthalene and 50.0 g (0.284 mol) of gallium (III) chloride were charged into a four-necked flask, then the
20 mixture was heated and stirred under reflux at 255°C for 12 hours. Thereafter, the reflux was stopped and the mixture was allowed to cool to a temperature of approximately 130°C, and thereafter was filtered under heating, and sprinkled and washed with 2000 ml of hot dimethylformamide (100°C-
25 DMF) and 1000 ml of DMF. The obtained cake was dispersed

again into 1500 ml of DMF, stirred and refluxed for 3 hours,
and thereafter was filtered under heating at 110°C,
thereafter sprinkled and washed with 1000 ml of hot DMF
(110°C) and 1000 ml of DMF. After repeating this step
5 twice, the obtained cake was washed with 1000 ml of
methanol and 1000 ml of water, thereafter dried at 70°C to
obtain 128.8 g of chlorogallium phthalocyanine ClGaPc
(yield: 73.5%).

10 Synthesis Example 5

Synthesis of chloroaluminum phthalocyanine

(A method described in Synthesis Example 1 of Japanese
Patent Kokai Publication No. H9(1997) 217020)

Phthalonitrile (180.0 g, (1.41 mol)), 900 ml of 1-
15 chloronaphthalene and 47.0 g (0.353 mol) of aluminum (III)
chloride were charged into a four-necked flask, and heated
and stirred under reflux at 240°C for 6 hours. Thereafter,
the reflux was stopped and the mixture was allowed to cool
to a temperature of approximately 130°C, and thereafter was
20 filtered under heating, sprinkled and washed with 1800 ml
of hot toluene (100°C), 80 ml of toluene and 900 ml of
acetone, and substituted with 100 ml of toluene. The
obtained cake was stirred and refluxed in 750 ml of toluene
for 3 hours, thereafter filtered under heating at 100°C,
25 and thereafter was washed with 1800 ml of hot toluene

(100°C), 180 ml of toluene and 900 ml of acetone, and the solvent was substituted with 400 ml of water. The obtained cake was added to 4500 ml of water and heat-dispersed at 70°C for 1 hour. After being filtered under heating, the
5 obtained cake was washed with 900 ml of acetone and 1000 ml of water, and dried at 70°C to obtain 187.6 g of chloroaluminum phthalocyanine ClAlPc (yield: 92.5%).

Synthesis Example 6

10 Chlorogallium phthalocyanine obtained in Synthesis Example 4 was dissolved in concentrated sulfuric acid and the acid pasting treatment was conducted. It is known that the product thus obtained is a mixture of hydroxygallium phthalocyanine (HOGaPc) and μ -oxo gallium phthalocyanine
15 dimer (PcGa-O-GaPc), as described in the Journal of Chemical Society of Japan, 12, 878, 1997.

Synthesis Example 7

Synthesis of tetrakis(tert-butyl)-titanylphthalocyanine

20 The same procedure as Synthesis Example 1 was conducted except that tert-butyl-phthalonitrile was employed instead of the starting material (phthalonitrile) in Synthesis Example 1 to synthesize tetrakis(tert-butyl)-titanylphthalocyanine $O=TiPc(t-Bu)_4$.

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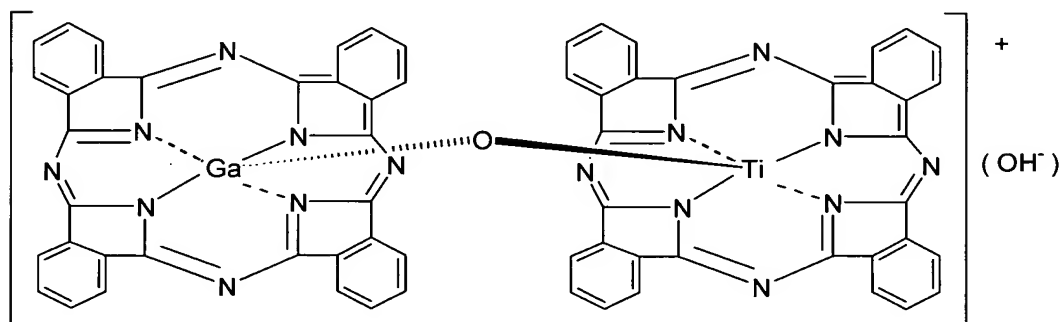
Synthesis Example 8Synthesis of tetrakis(tert-butyl)-chlorogallium
phthalocyanine

The same procedure as Synthesis Example 4 was
5 conducted except that tert-butyl-phthalonitrile was
employed instead of the starting material (phthalonitrile)
in Synthesis Example 4 to synthesize tetrakis(tert-butyl)-
chlorogallium phthalocyanine ClGaPc(t-Bu)₄.

10 Example 1Synthesis of μ -oxo bridged heterometal phthalocyanine
compound based on ClGaPc/OTiPc (1:1)

Concentrated sulfuric acid (358 g) was cooled to a
temperature of 5°C or less, and a mixture of 6.1 g (0.010
15 mol) of chlorogallium phthalocyanine and 5.7 g (0.010 mol)
of titanyl phthalocyanine was added thereto with keeping
the temperature, and was stirred at 5°C for 2 hours. This
mixture was dropped into 0.6L water and 1.4L of ice at 10°C
or less and dispersed for 2 hours. After standing for a
20 while, the mixture was filtered under reduced pressure, and
the obtained wet cake was sprinkled and washed with 2.0L of
water. The wet cake and 200 ml of water were charged into
a 3L beaker and dispersed at room temperature for 2 hours.
After being filtered under reduced pressure, 2.0L of water
25 was sprinkled on the obtained wet cake so as to wash. The

wet cake, 0.2L of water and 0.15L of 25%-aqueous ammonia were charged into a 1L separable flask and dispersed at room temperature for 6 hours. After being filtered under reduced pressure, 2.0L of hot water and 1.0L of ion-exchanged water were sprinkled on the obtained wet cake so as to wash. The wet cake was dried at 70°C to obtain 10.7 g of blue solid represented by the following formula. (yield: 91.0%).



The results of elemental analysis of this compound (PcGa-O-TiPc, molecular weight: 1175.64) are shown in Table 1.

Table 1

	C	H	N	Ga	Ti
Calculated Value	65.38	2.83	19.06	5.93	4.07
Found Value	66.01	2.49	18.11	6.00	3.65

An X-ray diffraction spectrum (XRD spectrum) of this compound is shown in Fig. 1. In addition, a mass spectrum of this compound by TOF-MS (time-of-flight mass spectrum)

is shown in Fig. 2. The mass spectrum by TOF-MS was conducted by using "KOMPACT MALDI III" under the condition of detection mode: POSITIVE, applied voltage: LOW (5KV) and flying mode: REFLECTION.

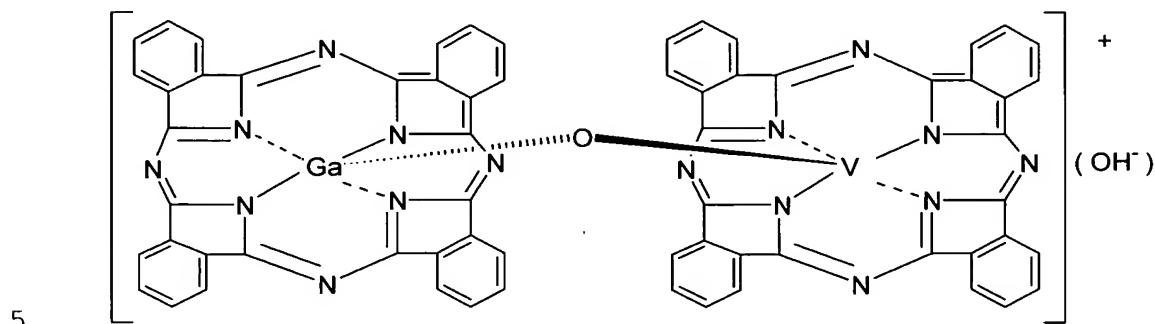
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Example 2

Synthesis of μ -oxo bridged heterometal phthalocyanine compound based on ClGaPc/OVPc (1:1)

Concentrated sulfuric acid (182 g) was cooled to a
10 temperature of 5°C or less and a mixture of 3.1 g (0.005 mol) of chlorogallium phthalocyanine and 2.9 g (0.005 mol) of vanadyl phthalocyanine was added thereto with keeping the temperature thereof, and was stirred at 5°C for 2 hours. This mixture was dropped into 0.3L water and 1.0L of ice at
15 10°C or less and dispersed for 2 hours. After standing for a while, the mixture was filtered under reduced pressure, and the obtained wet cake was sprinkled and washed with 2.0L of water. The wet cake and 200 ml of water were charged into a 3L beaker and dispersed at room temperature
20 for 2 hours. After being filtered under reduced pressure, 2.0L of water was sprinkled on the obtained wet cake so as to wash. The wet cake, 0.2L of water and 0.15L of 25%-aqueous ammonia were charged into a 1L separable flask and dispersed at room temperature for 6 hours. After being
25 filtered under reduced pressure, 2.0L of hot water and 1.0L

of ion-exchanged water were sprinkled on the obtained wet cake so as to wash. The wet cake was dried at 70°C to obtain 5.3 g of blue solid represented by the following formula (yield: 90.0%).



The results of elemental analysis of this compound (PcGa-O-VPc, molecular weight: 1178.72) are shown in Table 2.

Table 2

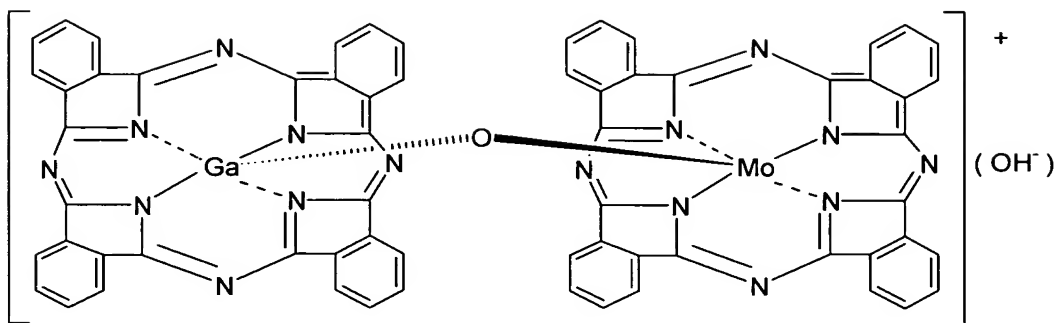
	C	H	N	Ga	V
Calculated Value	65.21	2.82	19.01	5.92	4.32
Found Value	66.71	2.33	18.71	5.84	4.36

10 An XRD spectrum of this compound is shown in Fig. 3. In addition, a mass spectrum of this compound by TOF-MS is shown in Fig. 4.

Example 3

15 Synthesis of μ -oxo bridged heterometal phthalocyanine compound based on ClGaPc/OMoPc (1:1)

Concentrated sulfuric acid (190 g) was cooled to a temperature of 5°C or less and a mixture of 3.1 g (0.005 mol) of chlorogallium phthalocyanine and 3.1 g (0.005 mol) of oxymolybdenum phthalocyanine was added thereto with
5 keeping the temperature thereof, and was stirred at 5°C for 2 hours. This mixture was dropped into 0.3L water and 0.9L of ice at 10°C or less and dispersed for 2 hours. After standing for a while, the mixture was filtered under reduced pressure, and the obtained wet cake was sprinkled
10 and washed with 2.0L of water. The wet cake and 0.9L of water were charged into a 2L beaker and dispersed at room temperature for 2 hours. After being filtered under reduced pressure, 1.5L of water was sprinkled on the obtained wet cake so as to wash. The wet cake, 0.3L of
15 water and 0.18L of 25%-aqueous ammonia were charged into a 1L separable flask and dispersed at room temperature for 6 hours. After being filtered under reduced pressure, 1.5L of hot water and 1.0L of ion-exchanged water were sprinkled on the obtained wet cake so as to wash. The wet cake (33.6
20 g) was dried at 70°C to obtain 5.0 g of blue solid represented by the following formula (yield: 81.7%).



The results of elemental analysis of this compound (PcGa-O-MoPc, molecular weight: 1223.72) are shown in Table 3.

5

Table 3

	C	H	N	Ga	Mo
Calculated Value	62.82	2.72	18.31	5.70	7.84
Found Value	63.99	2.72	18.35	6.26	7.69

Example 4

Synthesis of μ -oxo bridged heterometal phthalocyanine compound based on ClAlPc/OTiPc (1:1)

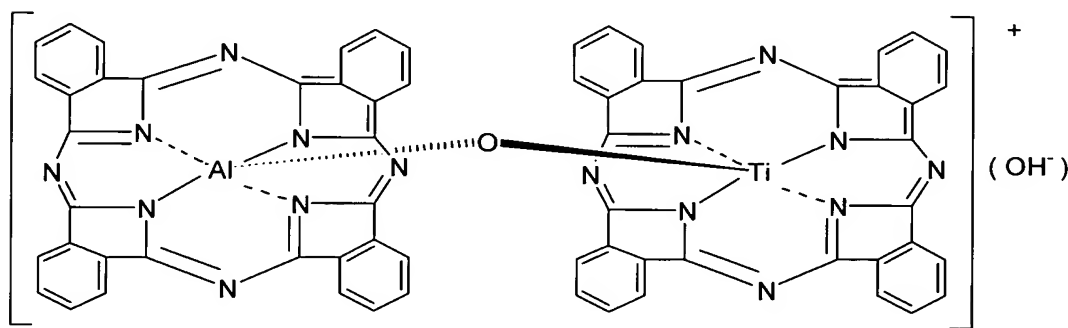
10

Concentrated sulfuric acid (176 g) was cooled to a temperature of 5°C or less and a mixture of 2.9 g (0.005 mol) of chloroaluminum phthalocyanine and 2.9 g (0.005 mol) of titanylphthalocyanine was added thereto with keeping the temperature thereof, and was stirred at 5°C for 2 hours.

15

The mixture was dropped into 0.4L water and 0.8L of ice at 10°C or less and dispersed for 2 hours. After standing for

a while, the mixture was filtered under reduced pressure, and the obtained wet cake was sprinkled and washed with 2.0L of water. The wet cake and 0.7L of water were charged into a 2L beaker and dispersed at room temperature for 2 hours. After being filtered under reduced pressure, 1.5L of water was sprinkled on the obtained wet cake so as to wash. The wet cake, 0.2L of water and 0.15L of 25%-aqueous ammonia were charged into a 1L separable flask and dispersed at room temperature for 6 hours. After being filtered under reduced pressure, 1.5L of hot water and 1.5L of ion-exchanged water were sprinkled on the obtained wet cake so as to wash. The wet cake (30.4 g) was dried at 70°C to obtain 4.8 g of blue solid represented by the following formula (yield: 84.8%).



The results of elemental analysis of this compound (PcAl-O-TiPc, molecular weight: 1132.90) are shown in Table 4.

Table 4

	C	H	N	Al	Ti
Calculated Value	67.85	2.94	19.78	2.38	4.23
Found Value	66.17	2.39	18.35	2.24	4.90

An XRD spectrum of this compound is shown in Fig. 5.

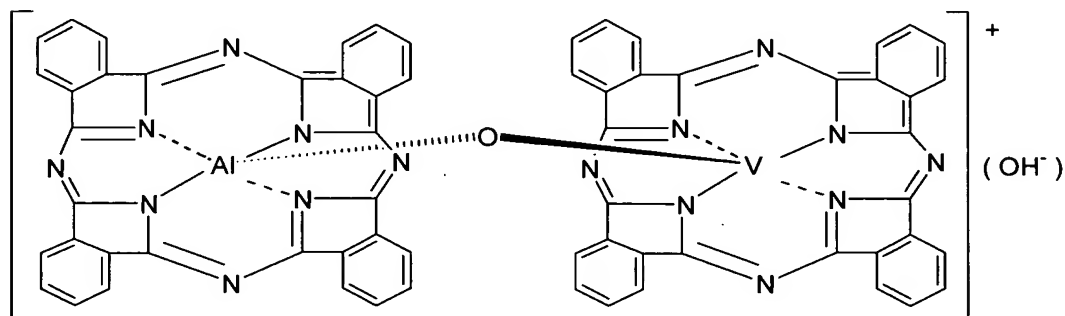
In addition, a mass spectrum of this compound by TOF-MS is shown in Fig. 6.

5 Example 5

Synthesis of μ -oxo bridged heterometal phthalocyanine compound based on ClAlPc/OVPc (1:1)

Concentrated sulfuric acid (352 g) was cooled to a temperature of 5°C or less and a mixture of 5.8 g (0.010 mol) of chloroaluminum phthalocyanine and 5.8 g (0.010 mol) of vanadyl phthalocyanine was added thereto with keeping the temperature thereof, and was stirred at 5°C for 2 hours. This mixture was dropped into 0.5L water and 1.5L of ice at 10°C or less and dispersed for 2 hours. After standing for a while, the mixture was filtered under reduced pressure, and the obtained wet cake was sprinkled and washed with 1.0L of water. The wet cake and 1.4L of water were charged into a 3L beaker and dispersed at room temperature for 2 hours. The wet cake, 0.4L of water and 0.2L of 25%-aqueous ammonia were charged into a 1L separable flask and dispersed at room temperature for 6 hours. After being

filtered under reduced pressure, 1.5L of hot water and 1.5L of ion-exchanged water were sprinkled on the obtained wet cake so as to wash. The wet cake was dried at 70°C to obtain 10.2 g of blue solid represented by the following
 5 formula (yield: 89.8%).



The results of elemental analysis of this compound (PcAl-O-VPc, molecular weight: 1135.98) are shown in Table
 5.

10 Table 5

	C	H	N	Al	V
Calculated Value	67.67	2.93	19.73	2.38	4.48
Found Value	69.43	2.49	19.14	2.20	4.58

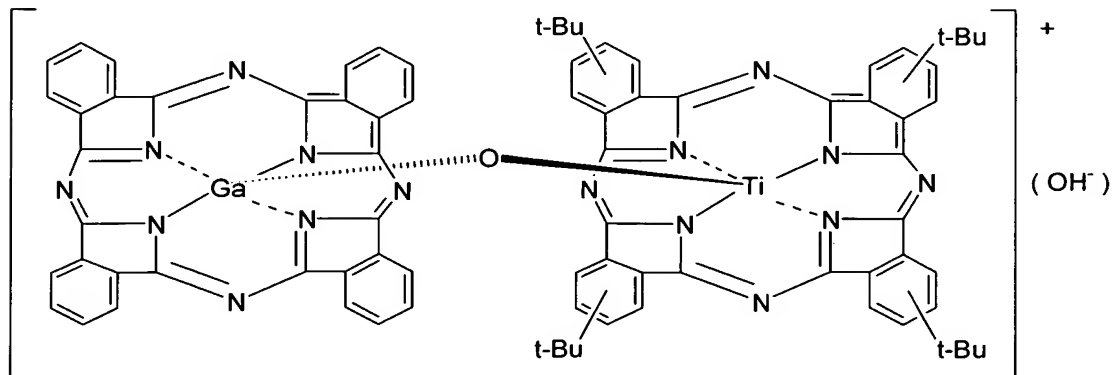
Example 6

Synthesis of μ -oxo bridged heterometal phthalocyanine compound based on ClGaPc/(tert-Bu)₄PcTi=O (1:1)

15 Concentrated sulfuric acid (74 g) was cooled to a temperature of 5°C or less and a mixture of 1.16 g (1.87

mmol) of chlorogallium phthalocyanine and 1.50 g (1.87
mmol) of (tetra-*tert*-butyl)titanylphthalocyanine was added
thereto with keeping the temperature thereof, and was
stirred at 5°C for 2 hours. This mixture was dropped into
5 0.15L water and 0.3L of ice at 10°C or less and dispersed
for 2 hours.

After standing for a while, the mixture was filtered under
reduced pressure, and the obtained wet cake was sprinkled
and washed with 0.5L of water. The wet cake and 0.65L of
10 water were charged into a 1L beaker and dispersed at room
temperature for 2 hours. The wet cake, 0.4L of water and
0.1L of 25%-aqueous ammonia were charged into a 1L
separable flask and dispersed at room temperature for 6
hours. After being filtered under reduced pressure, 0.5L
15 of hot water and 1.0L of ion-exchanged water were sprinkled
on the obtained wet cake so as to wash. The wet cake was
dried at 70°C to obtain 1.84 g of blue solid represented by
the following formula (yield: 70.2%).



The results of elemental analysis of this compound

(PcGa-O-TiPc(tert-Bu)₄, molecular weight: 1400.07) are shown in Table 6.

Table 6

	C	H	N	Ga	Ti
Calculated Value	68.63	4.68	16.01	4.98	3.42
Found Value	69.05	4.10	15.32	5.16	2.76

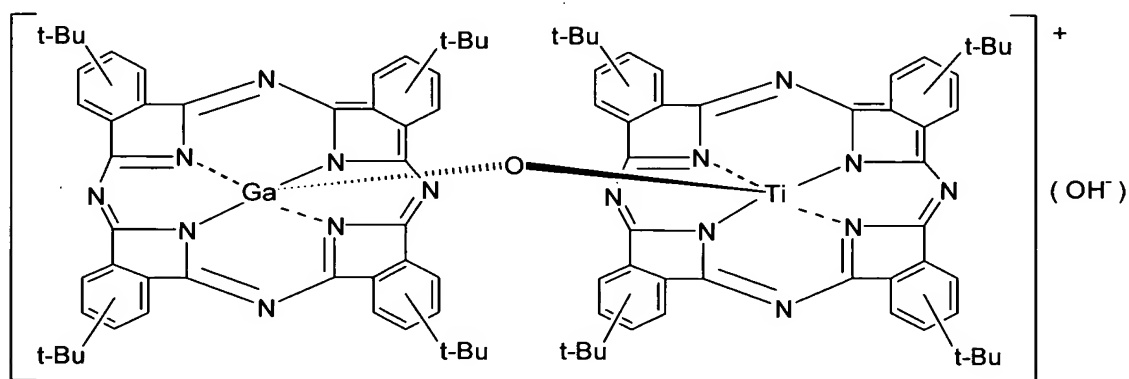
In addition, a mass spectrum of this compound by TOF-MS is shown in Fig. 7.

Example 7

Synthesis of μ -oxo bridged heterometal phthalocyanine compound based on (tert-Bu)₄PcGaCl/(tert-Bu)₄PcTi=O (1:1)

Concentrated sulfuric acid (71 g) was cooled to a temperature of 5°C or less and a mixture of 1.26 g (1.50 mmol) of (tetra-*tert*-butyl) chlorogallium phthalocyanine and 1.20 g (1.50 mmol) of (tetra-*tert*-butyl) titanylphthalocyanine was added thereto with keeping the temperature thereof, and was stirred at 5°C for 2 hours. This mixture was dropped into 0.2L water and 0.3L of ice at 10°C or less and dispersed for 2 hours. After standing for a while, the mixture was filtered under reduced pressure, and the obtained wet cake was sprinkled and washed with 1.8L of water. The wet cake and 0.4L of water were charged into a 1L beaker and dispersed at room temperature for 2

hours. The wet cake, 0.2L of water and 0.12L of 25%-aqueous ammonia were charged into a 1L separable flask and dispersed at room temperature for 6 hours. After being filtered under reduced pressure, 1.0L of hot water and 1.2L of ion-exchanged water were sprinkled on the obtained wet cake so as to wash. The wet cake was dried at 70°C to obtain 1.89 g of blue solid represented by the following formula (yield: 77.5%).



The results of elemental analysis of this compound (molecular weight: 1624.5) are shown in Table 7.

Table 7

	C	H	N	Ga	Ti
Calculated Value	70.98	6.02	13.80	4.29	2.95
Found Value	72.35	5.82	14.04	3.65	3.14

A mass spectrum of this compound by TOF-MS is shown in Fig. 8. In addition, a ^1H -HNR spectrum, a ^{13}C -NMR spectrum, an IR spectrum, a near-ultraviolet visible near-infrared absorption of this compound are shown in Fig 9, 10, 11 and

12, respectively.

Comparative Example 1

Synthesis of μ -oxo aluminum/gallium phthalocyanine dimer

5 (A method described in Example 1 of Japanese Patent Kokai
Publication No. 2000-219817)

Concentrated sulfuric acid (357 g) was cooled by ice-methanol to a temperature of 5°C or less and a mixture of 6.17 g (0.01 mol) of chlorogallium phthalocyanine obtained
10 in Synthesis Example 4 and 5.75 g (0.01 mol) of chloroaluminum phthalocyanine obtained in Synthesis Example 5 was added with keeping the temperature thereof, and was stirred at 5°C or less for 2 hours. This was poured onto 1400 g of ice/600 ml of water while being stirred at 10°C
15 or less, and further dispersed for 1 hour after the pouring was completed. After standing for a while, the supernatant was removed and filtered. The cake was washed with 2000 ml of water, and dispersed into 1800 ml of water and suction-filtered. The cake was washed with 800 ml of water. The
20 water-washed cake was added to 550 ml of hot water and 66 ml of 25%-aqueous ammonia and dispersed under reflux for 6 hours. After being filtered, the cake was washed with 600 ml of hot water (60°C) and 1650 ml of ion exchange water (IEW). When pH and conductivity of the filtrate are an
25 equal level to those of the ion exchange water, the cake

was dried at 70°C to obtain 10.5 g of blue solid (yield: 89.8%).

Then, 9.0 g of the obtained blue solid and 150 ml of o-dichlorobenzene were charged into a 300 ml flask, and the
5 obtained mixture was stirred at 170 to 180°C. This mixture was refluxed and stirred for 10 hours with removing water to be produced. After being filtered under heating at 130°C, the obtained wet cake was sprinkled and washed sequentially with 225 ml of hot DMF (110°C), 45 ml of DMF,
10 90 ml of methanol and 225 ml of IEW, thereafter the obtained cake was dried at 70°C to obtain 8.4 g (yield: 95%) of a solid including a μ -oxo aluminum/gallium phthalocyanine dimer (PcAl-O-GaPc) in a form of mixed polymorph.

Comparative Example 2

A sample was prepared by simply mixing titanyl
phthalocyanine (O=TiPc) obtained in Synthesis Example 1
with chlorogallium phthalocyanine (ClGaPc) obtained in
20 Synthesis Example 4 in equimolar amount.

The results of elemental analysis of this simple mixture are shown in Table 8.

Table 8

	C	H	N	Ga	Ti	Cl
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Calculated Value	64.37	2.68	18.77	5.84	4.01	2.98
Found Value	63.24	2.59	18.21	6.26	3.81	2.91

A mass spectrum of this simple mixture by TOF-MS is shown in Fig. 13.

5 Comparative Example 3

A sample was prepared by simply mixing titanyl phthalocyanine obtained in Synthesis Example 1 with a mixture of hydroxygallium phthalocyanine (HOGaPc) and μ -oxo gallium phthalocyanine dimer (PcGa-O-GaPc) obtained in
 10 Synthesis Example 6 in equimolar amount.

The results of mass spectrum by TOF-MS are shown in Tables 9 and 10, with reference to each of the ten compounds in Examples and Comparative Examples.

Table 9

Example No.	X-M1Pc	O=M2Pc	Condition	TOF-MS
Example 1	ClGaPc	TiOPc	Described in Example 1	[M-OH] ⁺ (1159.3) selective GaPc(1) GPL (very little)
Example 2	ClGaPc	VOPc	Described in Example 2	[M-OH] ⁺ (1162.6) selective GPL (very little)
Example 3	ClGaPc	MoOPc	Described in Example 3	[M-OH] ⁺ (1206.7) selective GaPc(1) GPL (very little)
Example 4	ClAlPc	TiOPc	Described in Example 4	[M-OH] ⁺ (1115.8) selective AlPc(m) APL (very little)
Example 5	ClAlPc	VOPc	Described in Example 5	[M-OH] ⁺ (1118.7) selective AlPc(1) APL (very little)
Example 6	ClGaPc	TiOPc(t-Bu) ₄	Described in Example 6	[M-OH] ⁺ (1383.6) selective GaPc(1)
Example 7	ClGaPc(t-Bu) ₄	TiOPc(t-Bu) ₄	Described in Example 7	[M-OH] ⁺ (1607.5) selective GaPc(1)

Table 10

Example No.	X-M1Pc	O=M2Pc	Condition	TOF-MS
Comparative Example 1	ClGaPc: ClAlPc =1:1	-	Described in Comparative Example 1 (mixed crystal)	M ⁺ (1137) GPL APL
Comparative Example 2	ClGaPc	TiOPc	Described in Comparative Example 2 (simply-mixing)	M ⁺ (1159.3, none) GaPc(1)
Comparative Example 3	HOGaPc, containing GPL	TiOPc	Described in Comparative Example 3 (simply-mixing)	M ⁺ (None) GPL/HOGaPc/GaPc(1) TiOPc (s)

Each abbreviation in Tables 9 and 10 is as follows.

ClGaPc: chlorogallium phthalocyanine

ClAlPc: chlorogallium phthalocyanine

TiOPc: titanyl phthalocyanine

5 VOPc: vanadyl phthalocyanine

MoOPc: oxymolybdenum phthalocyanine

GPL: μ -oxo gallium phthalocyanine dimer

APL: μ -oxo aluminum phthalocyanine dimer

HOGaPc: hydroxygallium phthalocyanine

10 (l): a large peak intensity

(m): a medium peak intensity

(s): a small peak intensity

15 M^+ and $[M-OH]^+$ in Tables 9 and 10 represents the
parent peak (PP) of a μ -oxo bridged heterometal
phthalocyanine compound dimer in TOF-MS.